

II. "On a New Series of Bodies Homologous to Hydrocyanic Acid."—

II. By A. W. HOFMANN, LL.D., F.R.S. Received August 31, 1867.

In a letter submitted to the Royal Society some weeks ago I directed attention to a new series of homologues and analogues of hydrocyanic acid, generated by the action of chloroform on the primary monamines. As a representative of this group of bodies, I described the cyanide of phenyl, the formation and the properties of which had been almost exclusively the subject of my researches.

I have followed up the study of these new bodies, which have become more and more attractive to me in proportion as I investigated their nature. Being formed in a well-defined reaction, endowed with properties quite unexpected, stable in certain cases, and of extreme alterability in others, capable of the most varied reactions that can be imagined, these bodies possess all the characters which invite a detailed examination. Thus I find myself at the threshhold of a long investigation, the results of which I beg permission to submit to the Royal Society in the order in which they present themselves.

Cyanide of Ethyl.

After having fixed in the phenylic group the general characters of the reaction, my attention was very naturally directed to the ethylic series. For this purpose, it was first necessary to procure ethylamine in rather considerable quantities. Happily in this case the liberal cooperation, so often experienced, of my friend Mr. E. C. Nicholson, was again at hand. Interesting himself with a cordiality, for which I cannot sufficiently thank him, in the continuation of my researches on the ethylic bases, Mr. Nicholson had placed at my disposal the product of the action of ammonia on iodide of ethyl produced in a single operation performed in one of his great autoclaves on 20 kilogs. of iodide of ethyl.

Thanks to the happy alliance between science and industry, which characterizes our times, I was thus enabled to study the transformation of ethylamine under the influence of chloroform on a rather large scale.

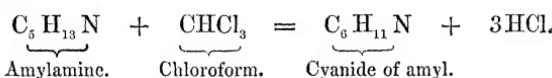
On gradually introducing a mixture of an alcoholic solution of ethylamine and chloroform into a retort containing powdered potassic hydrate, a most powerful reaction takes place; the mixture enters into ebullition, and a liquid distils over, the penetrating odour of which surpasses anything that it is possible to conceive. Besides the odoriferous body the product of the distillation contains ethylamine, chloroform, alcohol, and water, and a considerable number of rectifications are required in order to isolate the cyanide of ethyl from this mixture.

As the substance is rather volatile, the frequently repeated fractional distillations become a most painful operation, and more than once, while I have been engaged in these experiments, my laboratory has been almost inaccessible. Thus with a temperature of 30° I have found it desirable to

interrupt for the time the preparation in the pure state of the cyanide of ethyl, and to resume it at a more favourable season.

I was nevertheless curious to study, even now, a true homologue of cyanide of ethyl in order to compare its properties with those of cyanide of phenyl. The boiling-points of the amyllic compounds being within convenient limits, I was induced to select the amyl-series as presenting the greatest chance of success.

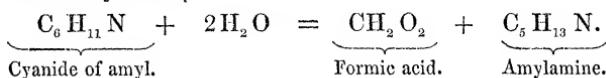
On submitting amylamine to the action of chloroform, the same phenomena are observed as in the analogous reaction between chloroform and aniline. One molecule of amylamine and one molecule of chloroform contain the elements of one molecule of cyanide of amyl and three of hydrochloric acid :—



The cyanide of amyl is a transparent colourless liquid lighter than water, insoluble in water, but dissolved by alcohol and ether, of an oppressive odour, resembling at the same time that of amyllic alcohol and of hydrocyanic acid. Its vapour possesses, in a still higher degree than that of the cyanide of phenyl, the property of producing on the tongue an insupportably bitter taste, and of giving rise in the throat to the sensation of suffocation, so characteristic of hydrocyanic acid.

The cyanide of amyl may be distilled without decomposition. It boils at 137° C. , that is, at a temperature 8° lower than the boiling-point of its isomer, capronitrile. It will be remembered that the boiling-point of cyanide of phenyl is lower than that of benzonitrile.

Under the influence of alkalies and acids, the cyanide of amyl behaves in the same manner as the phenylic cyanide. Though only slightly attacked by alkalies, it is decomposed by acids with a violence which is almost explosive; a short ebullition with water is sufficient to transform it into formic acid and amylamine:—



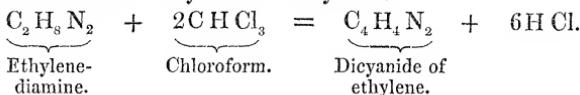
In order to fix this equation by numbers, I have carried out the reaction by means of dilute sulphuric acid. The formic acid was then distilled off and transformed into a sodium-salt, and analyzed as formate of silver; the residue in the retort furnished, on addition of an alkali, amylamine in considerable quantities. It was identified with that obtained from cyanate of amyl, both by the determination of its boiling-point and by the analysis of the platinum-salt.

The transformation of the cyanide of amyl, like that of the cyanide of phenyl, does not take place at a single step; intermediate combinations corresponding to methenylidiphenyldiamine and to phenylformamide are produced, but I have not yet obtained them in a state of purity.

I have designated the body described in this note by the name of *cyanide of amyl*; I am of course aware that the same name has been given to the substance produced by the action of cyanide of potassium on the sulph-amylates; but as the latter compound, in consequence of its transformation into caproic acid and ammonia, has a right to the name *capronitrile*, I have thought it desirable to distinguish, provisionally at least, the new product by the name of cyanide of amyl.

The examination of the cyanides of amyl and phenyl establishes in a positive manner the existence of a group of bodies isomeric with the nitriles derived from the ordinary alcohols and phenols.

I have not as yet pursued more minutely the study of the other terms of these groups; in fact the field opened by these new observations presents questions much more attractive. The existence of the new homologues of hydrocyanic acid allow us to foresee the formation of quite another series of homologues of cyanogen. These bodies will be produced by the action of chloroform on the diamines. Ethylene-diamine, for example, will thus be transformed into the dicyanide of ethylene;—



I am now occupied with the study of the action of chloroform on ethylene-diamine, and I propose shortly to inform the Royal Society whether experiment confirms the predictions of theory.

III. "On a New Series of Bodies Homologous to Hydrocyanic Acid."—

III. By A. W. HOFMANN, LL.D., F.R.S. Received September 7, 1867.

The new cyanides isomeric with the nitriles, which I have described in two previous communications, are not formed exclusively by the action of chloroform on the primary monamines. On perusing the papers describing the examination of the organic cyanides, we see at a glance that the chemists who investigated them have had in their hands at the same time the isomeric cyanides with which I am engaged.

In fact everyone who has distilled mixtures of sulphomethylate, sulphethylate, or sulphamylate of potassium with the cyanide of the same metal, will remember the repulsive odour possessed by the products so obtained. This odour only disappears in proportion as the product is purified, and especially after its treatment with acid, in order to remove the ammonia, and with oxide of mercury to separate the hydrocyanic acid.

Dumas, Malaguti, and Le Blanc, in their researches on the nitriles, mention the insupportable odour possessed by the cyanides obtained by the cyanide-of-potassium process; while the products obtained by the dehydration of the ammoniacal salts by means of phosphoric anhydride have a very agreeable aromatic odour.